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(54) METHOD FOR MANUFACTURING POLYMER WITH HIGH MOLECULAR WEIGHT

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CLAIM

A method for manufacturing a polymer with a high molecular weight, characterized by the fact that a high-molecular polymer with a weight average molecular weight of 1,000,000 or more is manufactured by bulk-polymerizing a radical polymerizable vinyl monomer with a light, using a polymerization initiator having a dithiocarbamate group represented by the following general formula (1).



(In the formula, R¹ and R² respectively represent hydrogen or alkyl groups having 1-10 carbons.)

Detailed explanation of the invention

Background of the invention

Industrial application field

The present invention pertains to a method for manufacturing a polymer with a high molecular weight.

More specifically, the present invention pertains to a manufacturing method for obtaining a polymer with a weight average molecular weight of 1,000,000 or more by bulk-polymerizing a radical polymerizable vinyl monomer, using a polymerization initiator having a dithiocarbamate group.

Prior art

It is broadly known that the molecular weight of a polymer has a general correlation with the properties such as chemical properties. In general, it is also known that if the molecular weight of a high-molecular material increases, its rigidity, aggregation force, wear resistance and chemical resistance are improved. Therefore, the demand of polymers with a high molecular weight has recently been in increased demand for the improvement of the performances in each field such as the improvement of the adhesive strength of adhesives and the creep characteristic, the improvement of the rigidity, elasticity, wear and chemical resistance of molding materials, and the improvement of the dispersibility in high-molecular compatibilizers.

As a polymerization method for manufacturing a polymer with a high molecular weight, a radical polymerization is generally appropriate, however it is also known that the molecular weight of the polymer manufactured by the radical polymerization depends on each factor such as polymerization temperature, initiator concentration, monomer concentration, solvent concentration, etc.

Here, the polymerization method in the radical polymerization is classified into bulk polymerization, solution polymerization, suspension polymerization, and emulsion polymerization by polymerization states.

However, the solution polymerization and the suspension polymerization cannot be used in manufacturing a polymer with a high molecular weight of 1,000,000 or more.

The reason for this is that in the solution polymerization, since a solvent acts as a chain transference during the polymerization reaction, it hinders the growth of a high molecular weight. On the other hand, it is known that the molecular weight of the high-molecular substance being obtained is increased with the decrease of the concentration of the polymerization initiator. In the suspension polymerization, since a stable polymerization reaction cannot be carried out unless the polymerization initiator concentration is 1 wt% or more to an ordinary monomer, a high-molecular polymer with a weight average molecular weight (M_w) of 1,000,000 or more cannot be obtained. Thus, this method cannot be used.

In the emulsion polymerization, it is well known that a polymer with a high molecular weight is obtained, however since a surfactant is used, the final properties such as water resistance are negatively affected. Also, since water is used as a medium, enormous labor and cost are required for drying.

Furthermore, in the bulk polymerization, as general polymerization initiation methods, there are thermal initiation, redox initiation, and optical initiation.

In general, a high-molecular substance with a high molecular weight is obtained with the decrease of the polymerization temperature, however since the reaction is carried out at a relatively high temperature in the thermal initiation, a polymer with a high molecular weight cannot be essentially obtained.

In the redox initiation, since the reaction can be advanced at a relatively low temperature, a polymer with a high molecular weight is obtained, however there is a possibility that it is a catalyst poison of a promoter as an essential element in accordance with monomers, so that the monomers being used are limited. Also, after completing the reaction, it is known that the residual promoter has a negative influence on the final properties such as hue, weather resistance.

OUTLINE OF THE INVENTION

Problems to be solved by the invention

In case the bulk polymerization of the optical initiation is carried out using an ordinary sensitizer such as azo compound, if the sensitizer has a low concentration, a polymer with a high molecular weight can be manufactured, however along with the considerable exothermic reaction, not only the reaction control is difficult, but the reactants lose the light transmittance along with a distinct foaming, so that the yield is lowered. Furthermore, the polymer generated by this method is frequently in a gel state and is insoluble in a solvent or loses the thermoplasticity.

Also, in case the bulk polymerization of the optical initiation is carried out without using the above-mentioned sensitizer such as peroxide and azo compound, and it is known that a polymer with a high molecular weight is obtained by decreasing the concentration of the polymerization initiator. In case the polymerization initiator is dissociated by heat, redox, or light, the life of radicals is very short, and if the heat source, promoter, or light source is removed, the polymerization initiator is deactivated. Furthermore, if the polymerization initiator concentration is too low, the reaction is not substantially advanced. On the other hand, it is known that a compound having a dithiocarbamate group has a radical polymerization initiation performance, however it has not been reported yet that a polymer with a high molecular weight of 1,000,000 or more is obtained using this initiator (Polymer Preprint, Japan, Vol. 32, No. 6, pp.1043 (1983)).

Means to solve the problems

The inventor reviewed these conventional problems in earnest to solve them, and as a result, it was discovered that these conventional problems could be overcome by adding a polymerization initiator having a dithiocarbamate group at low concentration to a radical polymerizable vinyl monomer with a very high purity and bulk-polymerizing it, so that a polymer with a high molecular weight could be obtained. Then, the present invention was completed.

In other words, the method for manufacturing a polymer with a high molecular weight of the present invention is characterized by the fact that a high-molecular polymer with a weight average molecular weight of 1,000,000 or more is manufactured by bulk-polymerizing a radical polymerizable vinyl monomer with a light, using a polymerization initiator having a dithiocarbamate group represented by the following general formula.



(In the formula, R¹ and R² respectively represent hydrogen or alkyl groups having 1-10 carbons.)

Effects of the invention

According to the manufacturing method of the present invention, a thermoplastic polymer with a high molecular weight, which has a high molecular weight, little gel portion, and is soluble in a solvent, can be manufactured by an inexpensive and easy method. Then, the polymer with a high molecular weight obtained by this method can be favorably used as adhesive, molding material, aggregator, and dispersant by utilizing its excellent performances.

DETAILED EXPLANATION OF THE INVENTION

Radical polymerizable vinyl monomer:

As the radical polymerizable vinyl monomer as a raw material of the present invention, any monomer having a radical polymerizability can be used. As examples of the monomer, there are lower alkyl (meth)acrylate such as methyl (meth)acrylate (methyl (meth)acrylate means methyl methacrylate or methyl acrylate; hereinafter, similarly applied), ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, and glycidyl ester (meth)acrylate; higher alkyl (meth)acrylate such as n-butyl (meth)acrylate, tert-butyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, lauryl (meth)acrylate, and stearyl (meth)acrylate; lower fatty vinyl ester such as vinyl acetate and vinyl propionate; higher fatty vinyl ester such as vinyl butyrate, vinyl caproate, 2-ethylhexane vinyl,

vinyl laurate, and vinyl stearate; aromatic vinyl type monomer such as styrene, vinyltoluene, and vinylpyrrolidone; vinyl type monomer containing an amide group such as (meth)acrylamide, N-methylol (meth)acrylamide, and N-methoxymethyl (meth)acrylamide; vinyl type monomer containing a hydroxyl group such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, and allyl alcohol; vinyl type monomer containing carboxylic acid such as (meth)acrylic acid, itaconic acid, crotonic acid, fumaric acid, and maleic acid; butadiene; vinyl chloride; vinylidene chloride; (meth)acrylonitrile; dibutyl fumarate; maleic anhydride; dodecyl succinic anhydride; (meth)acryl glycidyl ether; alkali metal salt, ammonium salt, and organoamine salt of a radical polymerizable unsaturated carboxylic acid such as itaconic acid, (meth)acrylic acid, and crotonic acid; radical polymerizable unsaturated monomer having a sulfonic acid group such as styrenesulfonic acid and these alkali metal salt, ammonium salt, and organoamine salt; quaternary aluminum salt being derived from (meth)acrylic acid such as 2-hydroxy-3-methacryloxypropyltrimethyl ammonium chloride; methacrylic acid ester of alcohol having a ternary amino group such as diethylamino ester methacrylate and their quaternary ammonium salt; vinyl monomer containing fluorine such as perfluoroalkyl (meth)acrylate and perfluoroalkylene (meth)acrylate, etc.

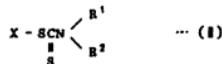
Also, in order to obtain the polymer with a high molecular weight of Mw 1,000,000 or more in the present invention, a high-purity vinyl monomer is preferably used as a raw material. The purity is usually 99.9% or more, preferably 99.99% or more. The raw material monomer with a high purity is usually obtained by distilling.

Also, according to the manufacturing method of the present invention, if two kinds or MORE OF vinyl monomers are used as raw materials as well as a homopolymer, a random copolymer can also be easily manufactured.

Polymerization initiator:

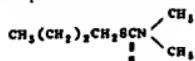
As the initiator having a dithiocarbamate group (functional group) represented by the above-mentioned general formula being used in the manufacture of the polymer with a high molecular weight of the present invention, as mentioned above, a monofunctional initiator having one functional group can be used, and a bifunctional or polyfunctional initiator having two or more functional groups can also be used.

As the usable monofunctional initiator, a compound represented by the following general formula

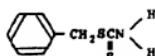


(In the formula, X represents an organic group, and R¹ and R² are respectively the same as R¹ and R² in the above-mentioned general formula (I).) Then, the organic group X may be a saturated or unsaturated hydrocarbon group and may also be a hydrocarbon group containing carbonyl group, ester group, or ether group.

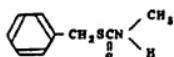
As detailed examples of the monofunctional initiator represented by the above-mentioned general formula (II), the following compounds are mentioned.



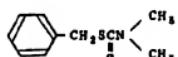
(n-butyl N,N-dimethyl dithiocarbamate)



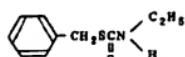
(Benzyl dithiocarbamate)



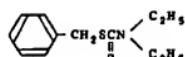
(Benzyl N-methyl dithiocarbamate)



(Benzyl N,N-dimethyl dithiocarbamate)

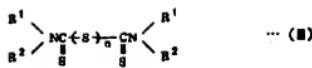


(Benzyl N-ethyl dithiocarbamate)

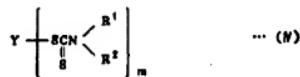


(Benzyl N,N-diethyl dithiocarbamate)

Also, as the usable polyfunctional initiator, a compound represented by the following general formula

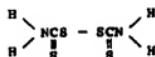


(In the formula, n represents an integer of 1-4, and R¹ and R² are respectively the same as R¹ and R² in the above-mentioned general formula (I).) and a compound represented by the following general formula

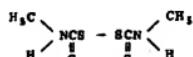


(In the formula, Y represents an organic group, R¹ and R² are respectively the same as R¹ and R² in the above-mentioned general formula (I), and m represents an integer of 2-40.) are mentioned.

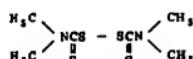
Then, as detailed examples of the compound represented by the above-mentioned general formula (III), the following compounds are mentioned.



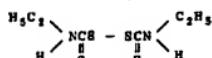
(Thiuram disulfide)



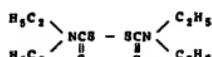
(N,N'-dimethyl thiuram disulfide)



(N,N,N',N'-tetramethyl thiuram disulfide)



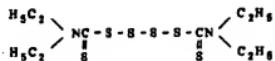
(N,N'-diethyl thiuram disulfide)



(N,N,N',N'-tetraethyl thiuram disulfide)

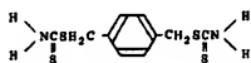


(N,N,N',N'-tetraethyl thiuram monosulfide)

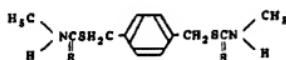


(N,N,N',N'-tetraethyl thiuram tetrasulfide)

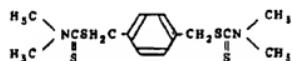
Also, as detailed examples of the compound represented by the above-mentioned general formula (IV), the following compounds are mentioned.



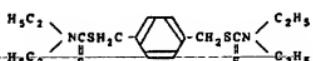
(p-xylene bis(dithiocarbamate))



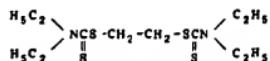
(p-xylene bis(N-methyl dithiocarbamate))



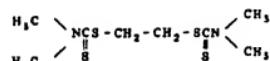
(p-xylene bis(N,N-dimethyl dithiocarbamate))



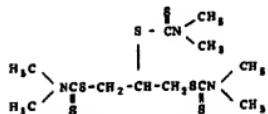
(p-xylene bis(N,N-diethyl dithiocarbamate))



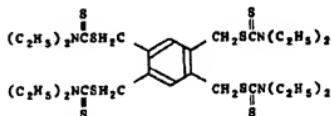
[1,2-bis(N,N-diethyl dithiocarbamyl)ethane]



[1,2-bis(N,N-dimethyldithiocarbamyl)ethane]

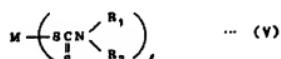


[1,2,3-tris(N,N-dimethyldithiocarbamyl)propane]



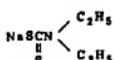
[1,2,4,5-tetrakis(N,N-diethyldithiocarbamylmethyl)benzene]

Also, a compound represented by the following general formula that can utilize a dithiocarbamate metal salt

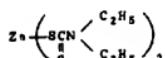


(In the formula, M represents monovalent to tetravalent alkali metals or alkaline-earth metals or transition metals, $\ell = 1-4$; and R^1 and R^2 are respectively the same as R^1 and R^2 in the above-mentioned general formula (I).) is mentioned.

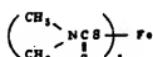
As detailed examples of the dithiocarbamate metal salt represented by the above-mentioned general formula (V), the following compounds are mentioned.



(Sodium N,N-diethyldithiocarbamate)



(Zinc N,N-diethyldithiocarbamate)



(Iron (II) N,N-diethyldithiocarbamate)



(Tellurium N,N-diethylidithiocarbamate)

Also, the polymerization initiator having a dithiocarbamate group of the present invention is used at usually 0.001-0.5 part by weight, preferably 0.005-0.1 part by weight, and especially preferably 0.01-0.05 part by weight to the radical polymerizable vinyl monomer at 100 parts by weight of the present invention.

Also, the initiator having a dithiocarbamate group used in the present invention can generally be synthesized with good efficiency by using an industrially manufactured reagent as it is or reacting an organohalide corresponding to sodium dithiocarbamate. For example, if p-xylene dibromide and sodium N,N-diethylidithiocarbamate are reacted, p-xylene bis(N,N-diethylidithiocarbamate) is obtained.

Light irradiation:

The monomer with a high molecular weight of the present invention is manufactured by activating a polymerization initiator having a dithiocarbamate group added into a monomer through heating or the irradiation of ultraviolet rays and initiating the polymerization of the monomer. In particular, it is preferable to initiate the polymerization by the ultraviolet irradiation, and at that time, an ordinary ultraviolet lamp may be used in the ultraviolet irradiation. The irradiation intensity, irradiation time, etc., depend on the monomer and the polymerization initiator being used, the ultraviolet rays are preferably in a range of 300-400 nm, and the ultraviolet lamp is 10-200 w/cm, preferably 30-120 w/cm. The irradiation time is 0.5-20 hours, and the gap between the lamp and the reactants is 5-100 cm. Also, the reaction temperature is usually -20-70°C, preferably 20-50°C.

Also, the average molecular weight can be controlled by the purity of the vinyl monomer as a raw material, the kind and amount of polymerization initiator, the irradiation intensity of ultraviolet rays, the irradiation time, and the polymerization temperature. Then, the polymer with a high molecular weight obtained by the polymerization can be easily purified by dissolving it once in a solvent and removing unreacted monomers and the polymerization initiator.

Structure of polymer with a high molecular weight:

The structure of the polymer obtained by the method of the present invention is different from the structure of the initiator being used. In other words, in case an initiator having one dithiocarbamate group in one molecule is used, a straight-chain polymer having a

dithiocarbamate group at one terminal is obtained, and in case an initiator having two dithiocarbamate groups in one molecule is used, a straight-chain polymer having dithiocarbamate groups at both terminals is obtained. Furthermore, in case an initiator having three or four dithiocarbamate groups in one molecule is used, a star-shaped polymer having dithiocarbamate groups at each terminal is obtained.

In any of these polymers, the repeating unit is a repeating unit of the monomer used.

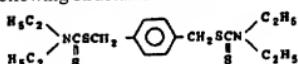
Then, the polymer obtained has almost no branch, and the degree of polymerization is about 10,000-100,000 on the average.

Application examples

Next, the present invention is mentioned in further detail by application examples and comparative examples, however the present invention is not limited by these examples.

Application Example 1

0.10 g p-xylene bis(N,N-diethyl dithiocarbamate) (hereinafter, simply abbreviated to "XDC") represented by the following structural formula



was completely dissolved in 500 g methyl methacrylate and put into 1 L reactor made of a Pyrex glass, and the residual gas in the reactor was sufficiently substituted by nitrogen, sealed, put at a position separated at 15 cm from 400 W ultraviolet lamp (H400 L mercury lamp made by Toshiba Corporation), and irradiated with ultraviolet rays for about 15 hours. After irradiating, when it was dissolved in 1,500 g toluene, it was completely dissolved, and no gel portion was formed. This polymer toluene solution was re-precipitated and purified in about 10 L hexane, and the precipitate was dried at 100°C for 12 hours under reduced pressure. As a result, the yield of the product was 461 g, the number average molecular weight converted into polystyrene based on a gel permeation chromatography (GPC) was 2,310,000, and same weight average molecular weight (Mw) was 4,730,000.

Application Example 2

The polymerization was carried out under the same conditions as those of Application Example 1 except for using 500 g styrene instead of 500 g methyl methacrylate of Application Example 1, and when the polymer was dissolved in toluene under the same conditions, it was completely dissolved, and no gel portion was formed. Also, the polymer solution was re-precipitated and purified in hexane under the same conditions and dried. As a result, the yield was 457 g, Mn was 2,450,000, and Mw was 5,100,000.

Application Example 3

The polymerization was carried out under the same conditions as those of Application Example 1 except for using 500 g methyl acrylate instead of 500 g methyl methacrylate of Application Example 1, and when the polymer was dissolved in toluene under the same conditions, it was completely dissolved, and no gel portion was formed. Also, the polymer solution was re-precipitated and purified in hexane under the same conditions and dried. As a result, the yield was 463 g, Mn was 2,380,000, and Mw was 4,700,000.

Application Example 4

The polymerization was carried out under the same conditions as those of Application Example 1 except for using 500 g vinyl acetate instead of 500 g methyl methacrylate of Application Example 1, and when the polymer was dissolved in toluene under the same conditions, it was completely dissolved, and no gel portion was formed. Also, the polymer solution was re-precipitated and purified in hexane under the same conditions and dried. As a result, the yield was 470 g, Mn was 2,470,000, and Mw was 4,800,000.

Application Example 5

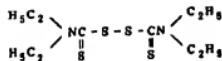
The polymerization was carried out under the same conditions as those of Application Example 1 except for using 0.060 g benzyl N,N-diethyl dithiocarbamate represented by the following structural formula



instead of 0.1 g XDC of Application Example 1, and when the polymer was dissolved in toluene under the same conditions, it was completely dissolved, and no gel portion was formed. Also, the polymer solution was re-precipitated and purified in hexane under the same conditions and dried. As a result, the yield was 455 g, Mn was 2,410,000, and Mw was 4,930,000.

Application Example 6

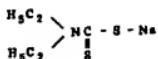
The polymerization was carried out under the same conditions as those of Application Example 1 except for using 0.074 g N,N,N',N'-tetraethyl thiuram disulfide represented by the following structural formula



instead of 0.1 g XDC of Application Example 1, and when the polymer was dissolved in toluene under the same conditions, it was completely dissolved, and no gel portion was formed. Also, the polymer solution was re-precipitated and purified in hexane under the same conditions and dried. As a result, the yield was 451 g, Mn was 2,490,000, and Mw was 4,970,000.

Application Example 7

The polymerization was carried out under the same conditions as those of Application Example 1 except for using 0.043 g sodium N,N-diethyl dithiocarbamate represented by the following structural formula



instead of 0.1 g XDC of Application Example 1, and when the polymer was dissolved in toluene under the same conditions, it was completely dissolved, and no gel portion was formed. Also, the polymer solution was re-precipitated and purified in hexane under the same conditions and dried. As a result, the yield was 451 g, Mn was 2,380,000, and Mw was 4,670,000.

Comparative Example 1

The polymerization was carried out under the same conditions as those of Application Example 1 except for using 0.1 g benzoyl peroxide instead of 0.1 g XDC of Application Example 1, and when the polymer was dissolved in toluene under the same conditions, a gel portion was partially generated, and the polymer was not completely dissolved. Furthermore, when the gel portion was re-precipitated and purified in hexane under the same conditions in a state in which the gel portion was included, the yield was 347 g, and since there was a large amount of insoluble portion, the GPC could not be measured.